Determination of the Molecular Structures of Bis(methylsilyl) Ether and Bis(dimethylsilyl) Ether in the Gas Phase by Electron Diffraction

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The molecular structures of the title compounds, $O(SiH_2Me)_2$ and $O(SiHMe_2)_2$, in the gas phase, have been determined by electron diffraction. The monomethylsilyl ether has at least two conformers, the major one (64%) having the methyl groups twisted by 124(4) and 58(8)° away from the positions in which the Si–C bonds are *trans* to O–Si bonds. Other important parameters (r_a) are: r(Si–C) 186.4(3), r(Si–O) 164.2(3) pm; SiOSi 143.0(6) and OSiC 109.7(5)°. In the dimethylsilyl ether the silyl groups are twisted by 101(8) and 41(4)° away from the symmetrical position in which both Si–H bonds are *cis* to O–Si bonds, so that the dimethylsilyl groups are staggered with respect to each other. Principal parameters (r_a) are: r(Si–C) 186.4(3), r(Si–O) 163.5(2) pm; SiOSi 148.4(9), OSiC 110.1(6), and CSiC 107.4(17)°.

When the structures of simple silyl derivatives of main-group elements were first studied it was found that bonds from silicon to nitrogen, oxygen, fluorine, *etc.* were short, compared with the sums of covalent radii, and that angles at nitrogen or oxygen were wide. In disilyl ether [1] the SiOSi angle found was 144.1(8)°, and the Si–O distance was 163.4(2) pm, much less that the expected value with an electronegativity-difference correction, 176 pm. In this study no allowance was made for possible shrinkage effects, and so there remained the possibility that in the average structure the angle was even greater than 144°, possibly even 180°.

More recently, analysis of the gas-phase Raman spectrum of disilyl ether [2] has shown that the potential for the SiOSi bending vibration has a minimum for an angle of 149°, with a barrier of 112 cm^{-1} at the linear configuration. In the solid phase [3] the SiOSi angle is almost the same as in the gas phase at 142.2(3)°, and the Si–O distances are also unchanged, despite the fact that there is a weak but specific interaction between one silicon and an oxygen atom of an adjacent molecule. In bis(trimethylsilyl) ether the SiOSi angles are 148(3)° in the gas phase [4] and 148.8(2)° in the crystalline phase,[3] suggesting that the potential minimum is not greatly affected by methyl substitution.

In this paper we report the structures of the ethers with monomethylsilyl and dimethylsilyl groups and compare them with the simple SiH_3 and trimethylsilyl ethers. We have also studied the conformations adopted, which are important, because of the asymmetry of the silyl groups.

Experimental

A sample of bis(monomethylsilyl) ether was prepared by reaction of chloro(methyl)silane with water, and was purified by fractional condensation *in vacuo*. Bis(dimethylsilyl) ether was made from chlorodimethylsilane and water, and was purified by distillation under nitrogen. The purity of each sample was checked by i.r. and n.m.r. spectroscopy.

Electron-diffraction scattering intensities were recorded on Kodak Electron Image plates, using the Cornell/Edinburgh diffraction apparatus,[5,6] with nozzle-to-plate distances of 128 and 286 mm and an accelerating voltage of *ca.* 44 kV. During exposures, samples and nozzles were maintained at room temperature (295 K). Data were obtained in digital form using a computer-controlled Joyce Loebl microdensitometer,[6] with the scanning programme described previously.[7] Electron wavelengths were determined from the scattering patterns of gaseous benzene, recorded on the same occasions as the sample data.

Calculations were carried out on ICL 2972 computers using established data-reduction [7] and least-squares refinement [8] programs. Weighting points used in setting up the off-diagonal weight matrices are given, together with other pertinent data, in Table 1. In all calculations the complex scattering factors of Schäfer *et al.*[9] were used.

Refinement

Molecular Models.—For refinements of the structure of $O(SiH_2Me)_2$ it was assumed that the two $OSiH_2Me$ groups were identical, with local C_{3v} symmetry for SiMe and local C_s symmetry for $OSiH_2C$, and the bisectors of the SiH_2 and OSiC angles were presumed to coincide. The structure was then determined by four bonded distances, four valence angles (OSiC, HSiH, SiCH, SiOSi), the OSiCH dihedral angle for one hydrogen atom of the methyl group, and two angles defining the conformations of the methyl substituents. These were defined to be zero for the position in which the Si–C bonds were *trans* to the further O–Si bonds, and positive for a clockwise twist when viewed from Si to O. The two angles could be constrained to be equal, giving overall C_2 symmetry, or equal and opposite, giving C_s symmetry.

Table 1. Weighting functions, correlation parameters, and scale factors

Compound	Camera height mm	Wavelength pm	Δs	$s_{min.}$	sw_1	sw_2	$s_{max.}$	Correlation parameter	Scale factor
			nm^{-1}						
$O(SiH_2Me)_2$	285.8	5.679	2	20	40	120	146	−0.071	0.905(11)
	128.4	5.682	4	60	85	300	348	0.102	0.929(20)
$O(SiHMe_2)_2$	285.9	5.680	2	20	40	120	146	−0.007	0.890(10)
	128.3	5.679	4	60	80	300	344	−0.324	0.855(13)

Table 2. Least-squares correlation matrix (× 100) for $O(SiHMe_2)_2$. Only elements ⩾40 are listed

a_2	a_3	a_5	a_6	a_8	u_5	u_6	u_8	u_{12}	u_{16}	k_1	k_2	
										42		r_2
−57		60	−67	−44	−42	56	41		42			a_1
	46				51	−90						a_2
						−63				−65		a_3
			−72	−53								a_5
				54					−40	−42		a_6
				−74			−58	58				a_7
											55	u_1
										49	63	u_2
											50	u_3
											49	k_1

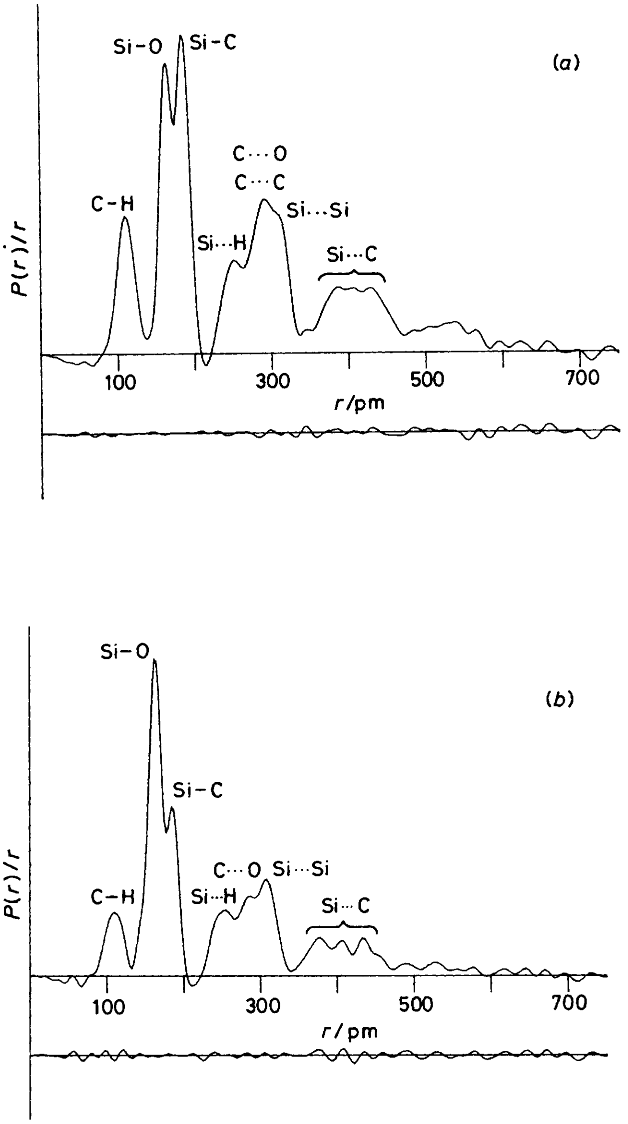

Figure 1. Observed and final difference radial-distribution curves, $P(r)/r$, for (*a*) $O(SiHMe_2)_2$ and (*b*) $O(SiH_2Me)_2$. In each case, before Fourier inversion, the data were multiplied by $s \cdot \exp[(-0.00002\, s^2)/(Z_{Si} - f_{Si})(Z_C - f_C)]$

Table 3. Molecular parameters

Independent distances/pm	$O(SiHMe_2)_2$	$O(SiH_2Me)_2$
r_1(Si–O)	163.5(2)	164.2(3)
r_2(Si–C)	186.4(3)	186.4(3)
r_3(C–H)	111.7(3)	111.3(5)
r_4(Si–H)	149.0 (fixed)	150.0(6)
Independent angles/°		
a_1(OSiC)	110.1(6)	109.7(5)
a_2(CSiC)/(HSiH)	107.4(17)	109.0 (fixed)
a_3(SiCH)	109.0(7)	107.8(10)
a_4(OSiH)	109.5 (fixed)	109.5 (fixed) [a]
a_5(SiOSi)	148.4(9)	143.0(6)
a_6(CH_3 twist)	30.2(25)	47.7 (fixed)
a_7(Si–O twist 1 [b])	101.3(84)	124.1(39) [c]
a_8(Si–O twist 2 [b])	−41.1(36)	58.3(75) [c]

[a] Dependent on other parameters: see text. [b] For definition see text. [c] Major conformer (64%) only. In the minor conformer these angles are 180 and 85°.

For $O(SiHMe_2)_2$ it was assumed that the two $OSiHMe_2$ groups were identical, with local C_{3v} symmetry for SiMe groups and C_s symmetry for $OSiHC_2$ groups. The basic structure was thus defined by the four bonded distances and the valence angles OSiC, CSiC, SiCH, OSiH, and SiOSi. The conformation of the methyl groups was assumed to be such that the $SiMe_2$ groups had local C_2 symmetry with the CH_3 twist angle defined to be zero when one C–H bond eclipsed an Si–O bond. The conformations adopted by the $SiHMe_2$ groups were defined by two angles, each taken to be zero when the Si–H bond was *cis* to the further O–Si bond. Both were positive for clockwise rotations, viewed from Si to O, and they could be constrained to be equal or equal and opposite, giving overall C_2 or C_s symmetry respectively, or to differ by a fixed amount.

$O(SiHMe_2)_2$ *Refinement.*—The radial-distribution curve for $O(SiHMe_2)_2$ [Figure 1(*a*)] shows clear peaks associated with the C–H, Si–O, and Si–C bonded distances, and also Si(C)H and Si···Si peaks. These three bond distances, angles SiCH and SiOSi, and five amplitudes of vibration, all refined satisfactorily. The C(Si)C and O(Si)C peaks overlapped at *ca.* 300 pm, and these distances were assumed to have the same amplitude of vibration. However the CSiC and OSiC angles were refined independently although the least-squares correlation matrix (Table 2) shows that they were strongly correlated.

The remaining features of the radial-distribution curve, above 350 pm, were less clearly defined, but provided information about the conformation of the molecule. Initially, all conformations with C_s and C_2 symmetry were investigated, but none satisfactorily reproduced the experimental data. Further refinements were tried with models in which angle 8 was con-

Table 4. Interatomic distances [a] and amplitudes (pm)

	$O(SiHMe_2)_2$		$O(SiH_2Me)_2$	
	Distance	Amplitude	Distance	Amplitude
d_1(Si–O)	163.5(2)	4.1(2)	164.2(3)	4.5(3)
d_2(Si–C)	186.4(3)	6.0(2)	186.4(3)	5.8(3)
d_3(C–H)	111.7(3)	8.5(3)	111.3(5)	9.0(6)
d_4(Si–H)	149.0 (fixed)	8.5 (fixed)	150.0(6)	6.7(9)
d_5(Si · · · Si)	314.7(7)	7.7(6)	311.4(6)	9.8(6)
d_6(C · · · O)	287.1(9)	10.7(13)	287.0(7)	9.5(10)
d_7(C · · · C)	300.4(25)			
d_8(Si · · · C)	448.4(14)	16.2(23)	388.3(32) [b]	18.7(28)
d_9(Si · · · C)	408.9(19)		407.3(13) [c]	
d_{10}(Si · · · C)	379.9(27)		434.0(17) [b]	9.3(22)
d_{11}(Si · · · C)	441.3(28)		451.2(10) [c]	
d_{12}(C · · · C)	553.6(29)	15.9(34)	553.9(42) [b]	35.8 (fixed)
d_{13}(C · · · C)	421.1(27)		543.4(17) [c]	
d_{14}(C · · · C)	547.3(17)			
d_{15}(C · · · C)	493.0(83)			
d_{16}(Si · · · H)	246.5(7)	12.5(7)	244.6(10)	13.3(9)
d_{17}(O · · · H)	255.4(3)	12.0 (fixed)	256.8(6)	10.4 (fixed)
d_{18}(C · · · H)	275.3(10)	12.0 (fixed)	275.6(6)	10.4 (fixed)

[a] Other non-bonded Si · · · H, O · · · H, C · · · H, and H · · · H distances were included in refinements, but are not listed here. [b] Major conformer only (64%). [c] Minor conformer only (36%).

strained to be either (180° – angle 7) or (60° – angle 7), and two minima were found that were investigated further. The two twist angles were allowed to refine separately, and for one structure obtained, with angles 182(8) and –33(7)°, the *R* factor (R_G) was 0.061. However, several refined parameters seemed unreasonable; for example, the CSiC angle was 103(2)°. Starting from the second minimum a much more reasonable solution was obtained, with R_G 0.055. The results of this refinement are given in Table 3, and the interatomic distances and amplitudes of vibration are listed in Table 4. It was not feasible to investigate all possible combinations of twist angles, but all combinations that seemed to be physically reasonable have been explored.

The difference radial-distribution curve [Figure 1(*a*)] shows no significant features, and so the possibility of a second conformer being present was not considered. Small amounts of forms other than that described cannot, of course, be ruled out.

The molecular-scattering intensity data are shown in Figure 2(*a*), and a view of the structure of $O(SiHMe_2)_2$ is shown in Figure 3.

$O(SiH_2Me)_2$ *Refinement.*—The main features of the radial-distribution curve for $O(SiH_2Me)_2$ [Figure 1(*b*)] are broadly similar to those in the curve for $O(SiHMe_2)_2$, but with changed intensities. For this compound it was possible to refine all the bond lengths and valence angles, with the exception of the angle OSiH, and most amplitudes of vibration associated with distances up to 320 pm were also refined.

The only major difficulties encountered were in attempts to define the conformation. When it was assumed that only one conformer was present, the best fit obtained had an *R* factor (R_G) of 0.067, and the Si–O twist angles refined to 131(3) and –124(5)°, so that the molecule almost had C_2 symmetry. However, the difference radial-distribution curve was very poor in the region of the non-bonded Si · · · C peaks (*ca.* 400 pm), and it can clearly be seen that the experimental curve has at least three or four contributions in this area. The model was therefore modified to allow inclusion of a variable proportion of a second conformer, differing from the first only in the twist angles around the Si–O bonds. These angles were set so that the Si · · · C distances in the second form coincided with the peak at 407 pm and the shoulder at *ca.* 450 pm, and the optimum proportions of the two forms were found by studying the variation of *R* factor with composition. In the best refinements, for which R_G was 0.060, there was 64(8)% of a

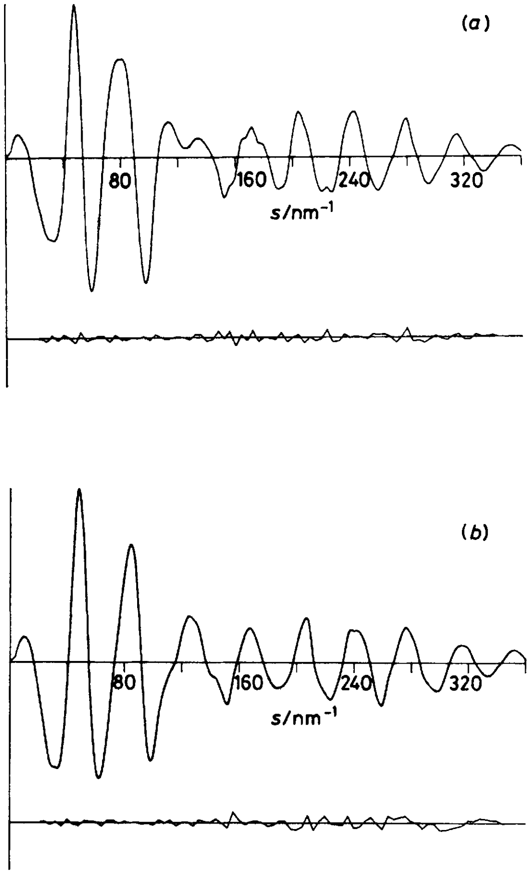

Figure 2. Observed and final weighted difference combined molecular-scattering intensities for (*a*) $O(SiHMe_2)_2$ and (*b*) $O(SiH_2Me)_2$

Table 5. Least-squares correlation matrix (× 100) for $O(SiH_2Me)_2$. Only elements ⩾40 are listed

r_3	a_1	a_3	a_5	a_7	a_8	u_4	u_6	u_{10}	u_{16}	k_1	k_2	
			−51			−71						r_1
	−44	−45								46		r_2
42									−47	−49	−41	r_4
		56		−49	−49				45			a_1
							−57			−52		a_3
					42			41				a_7
						56				45	55	u_1
											41	u_2
							61					u_5
								44				u_8
											52	k_1

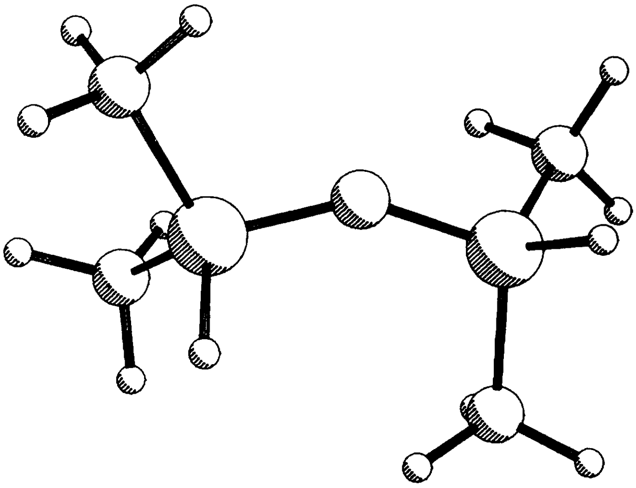

Figure 3. Perspective view of a molecule of $O(SiHMe_2)_2$

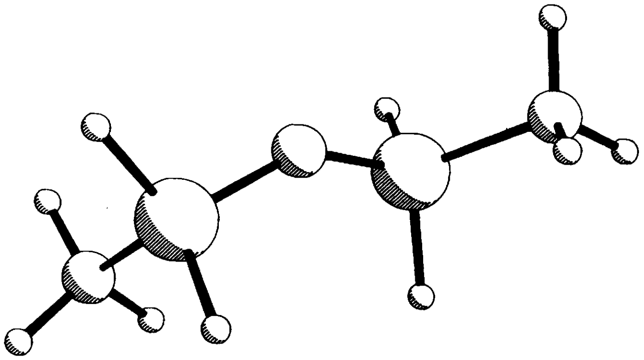

Figure 4. Perspective view of the major conformer of $O(SiH_2Me)_2$

conformer with twist angles of 124(4) and 58(8)°, and 36% of a form with angles 180 and 85°. These Si ··· C peaks could not be fitted so well by any other pair of conformers. The results of this refinement are given in Tables 3 and 4, and the least-squares correlation matrix is in Table 5. Molecular scattering data are shown in Figure 2(*b*). The difference radial-distribution curve [Figure 1(*b*)] still shows small but significant discrepancies around 400 pm, and it is probable that there are other conformers present, possibly with other combinations of the same four twist angles. We are fairly confident that what we have described as the major species (depicted in Figure 4) really is present, and that there are substantial amounts of one or more different species.

Table 6. Geometrical parameters for silyl ethers

Compound	State	r(Si–O)/pm	Angle (SiOSi)/°	Ref.
$O(SiH_3)_2$	Gas	163.4(2)	144.1(8)	1
	Solid	163.1(6)	142.2(3)	3
$O(SiH_2Me)_2$	Gas	164.2(3)	143.0(6)	
$O(SiHMe_2)_2$	Gas	163.5(2)	148.4(9)	
$O(SiMe_3)_2$	Gas	163.1(3)	148(3)	4
	Solid	162.6(5)	148.8(2)	3

Discussion

The most striking feature of the structures of the silyl ethers, which are compared in Table 6, is the insensitivity of Si–O distance and SiOSi angle to methyl substitution. Apart from a small increase in angle in the compounds with four or six methyl groups, which may be attributed to interactions between the two ends, there are no significant differences for these parameters, even when solid- and gas-phase structures are considered. Moreover, the angles at the central atoms of the isoelectronic species $Me_3PNSiMe_3$ [10] and Me_3PCPMe_3 [11] are 144.6(11) and 147.6(5)° respectively. It would be a great coincidence if these angles, none of which is corrected for shrinkage effects, should lie so close, if in fact the average angles are substantially greater, with large-amplitude bending vibrations. Thus there is circumstantial evidence, for this group of ethers, that there are potential minima for angles of *ca.* 145°, and that substantial distortion from this angle is not easy. With other substituents the situation may be quite different. It should be noted that $O(SiPh_3)_2$ has a linear SiOSi unit in the solid phase,[12] and that the angle in the isoelectronic $N(PPh_3)_2^+$ ion may lie between 134 [13] and 180°.[14]

The conformations adopted by the methylsilyl ethers are also of interest. In the gas phase [4] the trimethylsilyl groups in $O(SiMe_3)_2$ are twisted 30° away from the positions in which they are staggered with respect to the further O–Si bonds, with overall C_2 symmetry. If this structure is viewed along the Si ··· Si direction, the trimethylsilyl groups are seen to be fully staggered with respect to each other. In the solid phase [3] this relationship is retained, but with respect to the oxygen atom one group is twisted by 14°, and the other 46°. Similarly, in $O(SiHMe_2)_2$ the $SiHMe_2$ groups are staggered with respect to one another (in one of two possible arrangements), but are twisted by 19 and 41° with respect to the oxygen atom [Figure 5(*a*)]. In the major conformer of $O(SiH_2Me)_2$ one methyl group is twisted by 58° away from the oxygen atom, when viewed along the Si ··· Si axis, while the other is twisted 124°,

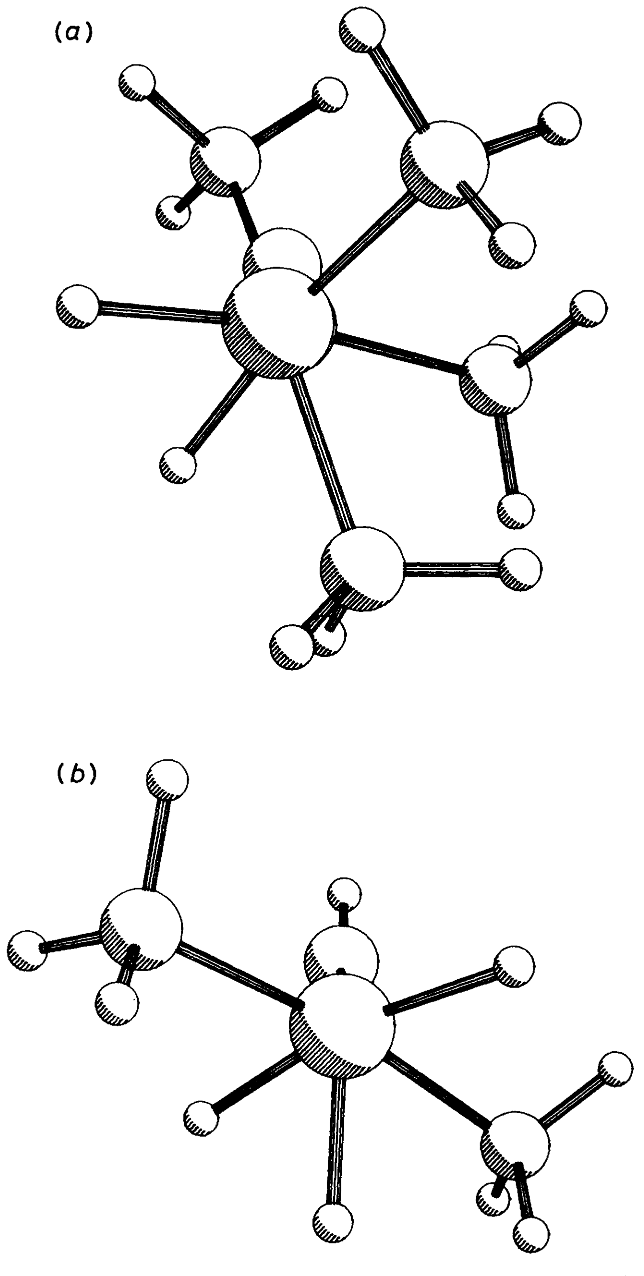

Figure 5. Views of (*a*) $O(SiHMe_2)_2$ and (*b*) $O(SiH_2Me)_2$ along their Si · · · Si axes

so that an Si–H bond almost eclipses the oxygen atom [Figure 5(*b*)]. Thus in every case the two $Si(H/R)_3$ groups are almost perfectly staggered with respect to each other, but there is no consistent relationship if orientations about Si–O bonds are considered. We therefore tentatively suggest that rotation about the Si–O bond is fairly unrestricted. It may be noted that in the solid phase of $O(SiH_3)_2$[3] there is a single short intermolecular contact between each oxygen and a silicon atom of a neighbouring molecule, so that each oxygen atom approaches planar three-co-ordination. This interaction is said to reflect weak donation of an electron pair from oxygen to silicon. It therefore seems that in these ethers the oxygen behaves as a planar group with one stereochemically effective lone pair of electrons and that consequently rotation about an Si-O bond involves a low six-fold barrier, with three energy minima in respect of the lone pair of electrons and three in respect of the other SiR_3 group.

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